

**“Fundamentals of Curing Elastomers
with Peroxides and Coagents III”:
Blending Coagents to Optimize Processing,
Vulcanization, and the Physical Properties
of Rubber Compounds”**

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ABSTRACT

Previous work in the series has demonstrated the addition of coagents affects both the quantity and quality of crosslinks in peroxide-cured elastomeric compounds. Compound vulcanization kinetics and ultimate physical properties were dictated by structure-property relationships unique to the different classes of coagents. In addition, it was shown that the relative impact of coagent addition correlates not only to coagent structure, but also the composition of the elastomer being cured.

In the present study, the concept of coagent blending is explored. While previous work has concentrated on establishing the effect of individual coagent structure on final properties, new data demonstrates that binary blends of coagents can act synergistically to balance multiple processing and cured physical properties. By blending certain classes of coagents, it may be possible to optimize physical properties that would be mutually exclusive if only working with a single coagent.

Specific examples define the blending rules in operation. By blending Type I and Type II coagents, scorch safety can be extended without a loss in tensile properties. Blends of metallic monomers and liquid monomers can produce adhesion while maintaining compression set. Processing properties can be modified while independently adjusting compound hardness by blending coagents with various functionalities. The utility of coagent blending is demonstrated in NBR, EPDM, HNBR, CM, and FKM model formulations.

INTRODUCTION

The use of coagent products in the radical vulcanization of elastomers is well established, and the fundamental nature of coagent materials has been explored. Through model reactions and analysis of *in-situ* derived networks, previous work has highlighted the fundamental chemistry and mechanisms of radical cure using allyl ester, allylic, and (meth)acrylate ester functional monomers.¹ Other work has determined the comparative activity of a wider group of monomeric and polymeric coagents through empirical studies.² Building on the theme, a subsequent study has looked at comparative coagent reactivity as a function of the host elastomer.³ It was shown that the ultimate physical properties of the cured network can be predicted by considering not only coagent structure but also the composition and microstructure of the elastomer being cured.

Structure-property relationships have been established for a wide selection of commercially available monomeric and polymeric coagent classes and grades. In the effort to properly define the chemistry and mechanistic contributions of the coagent types, most academic studies have considered only individual coagent grades. While a majority of commercial processes utilize a singular coagent grade to impart selected properties to a rubber formulation, a minority of cases takes advantage of coagent blends to optimize the critical properties of the rubber compound.

The goal of the current study is to determine the interaction between coagents when formulated together as binary blends in several peroxide cured compounds. The impact of coagent blending on the processing, cure kinetics, and ultimate physical properties of the compounds will be quantified. It will be shown that in most cases the effects of coagent blending are additive; it is possible to optimize separate compound properties that would be mutually exclusive if only considering a single coagent grade. Specific examples highlight the interactions. Blends of metallic monomers and liquid monomers can produce adhesion and increased tear strength while maintaining compression set. Processing properties can be maintained while independently adjusting cured properties by blending liquid coagents with various functionalities. By blending Type I and Type II coagents, scorch safety can be extended without a loss in tensile properties. The balance of modulus and elongation can be optimized. The utility of coagent blending will be demonstrated using peroxide cured NBR, EPDM, HNBR, CM,

and FKM model formulations. Blending guidelines will be established based on the experimental data provided.

EXPERIMENTAL

Materials

Table I outlines the commercially available coagent grades used in the study. They are available from Cray Valley Company, Inc. and used as received. For the purposes of discussion, the term (meth)acrylates will be used to describe the class of coagents covering the acrylate and methacrylate liquid and metallic monomer classes. Both dicumyl peroxide (Di-Cup® 40KE, Geo Specialty Chemicals) and 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane (Varox® DBPH 50, R.T. Vanderbilt Company, Inc.) curing agents were used at 3 phr and 1.5 phr active peroxide, respectfully. Table II provides a summary of the elastomer grades used to produce the model compound formulations. The NBR, EPDM, HNBR, CM, and FKM model compound formulations are provided in the Appendix.

Table I. Coagent grades and abbreviations.

GRADE	DESCRIPTION	ABBREVIATION	FORM	TYPE
	monofunctional methacrylate ester	MMA	liquid	I
	trifunctional methacrylate ester	TMA	liquid	I
	trifunctional acrylate ester	TA	liquid	I
SR634	zinc dimethacrylate	ZDMA	solid	I
SR633	zinc diacrylate	ZDA	solid	I
	phenylene dimaleimide	PDM	solid	I
	triallyl cyanurate	TAC	liquid	II
	triallyl isocyanurate	TAIC	liquid	II
Ricon® 154	high vinyl polybutadiene resin	HVPBD	liquid	II

Table II. Elastomer grades formulated in model compounds.

ELASTOMER TYPE	ASTM DESIGNATION	COMMERCIAL GRADE
nitrile rubber	NBR	Nipol® DN 3335, Zeon Chemicals
hydrogenated nitrile rubber	HNBR	Zetpol® 2010L, Zeon Chemicals
ethylene propylene diene rubber	EPDM	Nordel™ IP4640, Dow Chemical
chlorinated poly(ethylene)	CM	Tyrin™ 0136, Dow Chemical
fluorocarbon rubber	FKM	Viton® GF-S, DuPont Elastomers

Rubber Compounding

A set of compound evaluations was conducted using various coagents in model carbon black-filled formulations based on commercial elastomers. To limit systematic error derived from the mixing step, masterbatches containing all ingredients except the coagent and peroxide were prepared in an internal mixer to which the curatives were later added on a two-roll mill. Curative incorporation time was approximately 7 minutes at an average mixing temperature of 85°C. In each formulation, the selected coagents were evaluated at a constant total phr; blend ratios were prepared as percentages of the fixed phr loading. For the EPDM, CM, NBR and HNBR formulations, dicumyl peroxide was used; for the

FKM formulation, 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane initiated cure. For some formulations a control compound using no coagent (peroxide only) was included for comparison.

Physical Testing

Processing. A moving die rheometer (MDR, TechPro MDPT) was used to test uncured viscosity as determined by minimum torque (M_L) value prior to the onset of vulcanization according to ASTM D 5289. In addition, uncured dynamic shear modulus (G' at 100°C, 8.33 Hz, 15% strain, MDR) was used a second measure of processing characteristics.

Cure kinetics. An MDR was also used to determine the extent of cure and cure kinetics according to ASTM D 5289. The cure temperature was 160°C for compounds formulated with dicumyl peroxide and 180°C for The FKM compounds cured using 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane. Cure rheometry was conducted using an arc deflection of 0.5°. Cure times were sufficiently long to ensure near complete decomposition of the peroxide at the given cure temperatures (35 minutes for dicumyl peroxide, 15 minutes for 2,5-dimethyl-2,5-di-*t*-butyl-peroxyhexane).

Tensile and compression properties. Physical testing was performed on samples cured in a press under the same temperature and time conditions outlined above. Tensile and tear data was acquired on a tensile machine (Thwing-Albert Materials Tester) following ASTM D 412 and D 624(C). Compression set was evaluated after heating at 100°C for 22 hours following ASTM D 395 (200°C for FKM model).

Adhesion. Adhesion to metal substrates was evaluated using two geometries. Lap shear adhesion to brass coupons was measured using ASTM D 816, and pull-out adhesion to brass coated steel cord was measured using according to ASTM D 2229. Failure at the metal-rubber interface was assessed by using a subjective scale of 0 through 5, where 0 indicates no rubber coverage (adhesive failure) and 5 represents complete coverage (total cohesive failure).

RESULTS AND DISCUSSION

There are many possible combinations of coagent blends given the breadth of commercially available monomeric and polymeric grades. The goal of the experimental work is to demonstrate the potential use of coagent blends in peroxide cured compounds for a variety of standard rubber applications. The current study provides a survey of several binary blends. In each example two representative coagents were blended across a range of blend ratios while the overall coagent loading was fixed. Key uncured and cured physical properties were then measured and presented as a function of coagent blend ratio. In most cases there was high correlation between physical properties and blend ratio, establishing a predictable trend.

The examples are divided into groups based on coagent types, which are defined by molecular structure and cure activity. Type I coagents are highly reactive, altering both the rate and state of cure. Type II coagents are less reactive and primarily increase the state of cure, with minimal effect on cure rate. In the first section, blends of Type I coagents were considered. The ability to generate cured-in-place adhesion or improve tear properties while balancing other physicals was demonstrated with blends of zinc-based (meth)acrylate (metallic monomers) and traditional liquid (meth)acrylate monomers. Also, the role of liquid coagents as reactive processing aids was studied. Blends of multifunctional (meth)acrylate liquid coagents can provide plasticity in the uncured state while independently controlling ultimate compound properties such as hardness.

A second section highlights blending Type I monomers with Type II monomers and polymeric coagents. Again, the ability to increase adhesion to metal substrates while maintaining other tensile and compression properties was again examined. Other blends demonstrate how Type II coagents can be used to mitigate the decrease in scorch safety associated with Type I monomers.

Blending Type I Coagents

Metallic monomers blended with liquid monomers. When used as coagents, the zinc salts of acrylic and methacrylic acid impart unique physical properties to the cured network. The incorporation of zinc diacrylate (ZDA) or zinc dimethacrylate (ZDMA) as coagents into a composite can lead to high adhesive strength when it is cured against a metal substrate.⁴ The metallic monomers generate a heterogeneous crosslink density comprised of domains of coagent-rich structures which can interact with metal oxides on the substrate surface. The ionic nature of the linkages has also been cited as imparting improved flex fatigue and increased tear properties.^{5,6,7} The ability of the ionic linkage to reorganize and relieve stress under strain may account for the improved fatigue properties, but this mechanism, in conjunction with a heterogeneous crosslink density, can also lead to increased permanent set. As a comparison, the liquid (meth)acrylate monomers, which contain stronger covalent bonds, decrease compression set effectively.

A first example demonstrates the structure-property relationships governing both ZDMA and liquid trimethacrylate (TMA) coagents and compares the relative effects of blending ratio on different cured physical properties. Figure 1 provides tear strength and compression set data as a function of blend ratio for increasing amounts of ZDMA in a TMA/ZDMA blend ratio at a constant 10 phr coagent loading in the ethylene-propylene-diene rubber (EPDM) model formulation. Tear strength increased linearly as a function of the percentage of ZDMA in the blend, while compression set also increased. Figure 2 indicates that modulus was constant across the blend ratio spectrum. Figures 3 and 4 provide pull-out force and lap shear strength respectively, using brass substrates. Adhesion was also affected by the ZDMA concentration; pull-out force increased rapidly, achieving cohesive failure (full rubber coverage) at 40% blend ratio. Similarly, lap shear adhesion reached a maximum of force and rubber coverage at 40% ZDMA in the blend. As cohesive failure was achieved in both adhesion tests at approximately 40 phr % ZDMA in the blend, a compound formulated at this coagent ratio would only increase compression set by approximately 20% (based on the TMA data point), compared to a 100% compression set increase if only ZDMA was used as the coagent. A similar argument could be made for a tear and flexural fatigue/compression set balance.

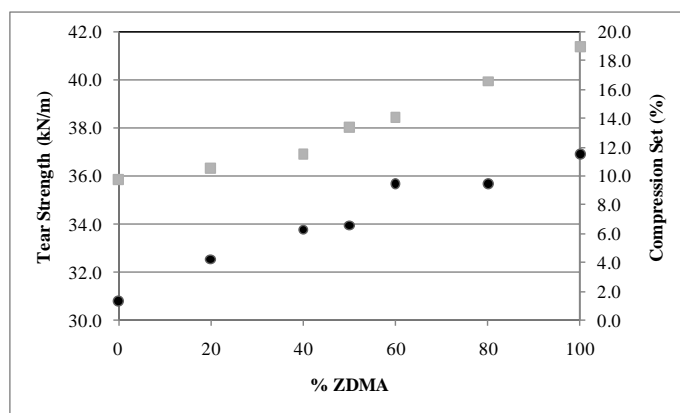


Figure 1. Tear strength (●) and compression set (■) as a function of phr % ZDMA in a TMA/ZDMA blend; 10 phr total coagent in the EPDM model formulation.

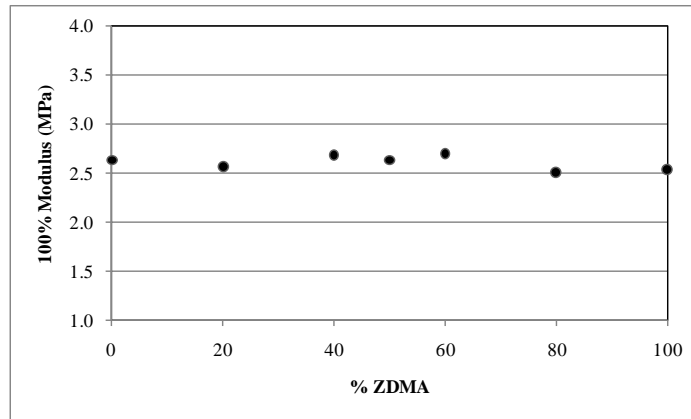


Figure 2. Modulus at 100% strain as a function of phr % ZDMA in a TMA/ZDMA blend; 10 phr total coagent in the EPDM model formulation.

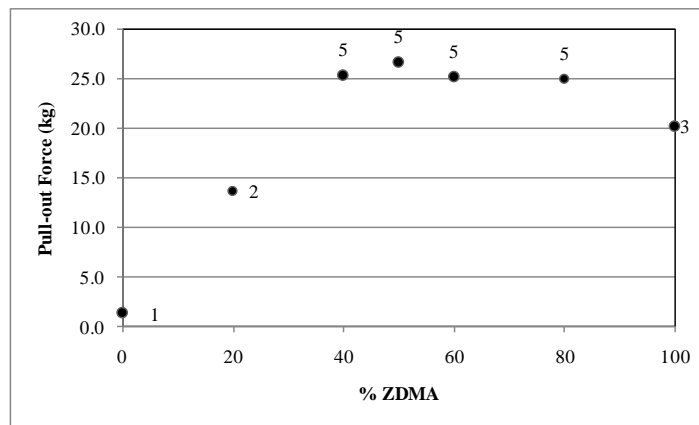


Figure 3. Pull-out adhesive force as a function of phr % ZDMA in a TMA/ZDMA blend; 10 phr total coagent in the EPDM model formulation; brass-coated steel cord substrate. Rubber coverage scale: 0 = no rubber coverage, 5 = total rubber coverage.

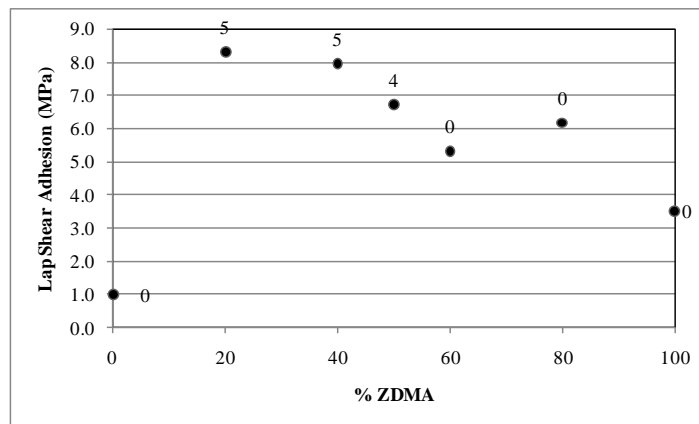


Figure 4. Lap shear strength as a function of phr % ZDMA in a TMA/ZDMA blend; 10 phr total coagent in the EPDM model formulation; brass coupon substrates. Rubber coverage scale: 0 = no rubber coverage, 5 = total rubber coverage.

A second example shows a similar trend using the acrylate analogues to the above coagents. Again, the model EPDM formulation was used and coagent loading was held at a constant 10 phr. Figure 5 provides tear strength and compression set data as a function of phr % ZDA in triacrylate (TA)/ZDA blends. The trends were similar to the above example based on methacrylates. Modulus data is given in Figure 6, and again is constant across the blend spectrum. Note that the absolute values of tear strength and modulus were generally higher at a given blend ratio compared to the methacrylate example, while compression set was comparable. Figure 7 shows the effect of metal acrylate coagents on adhesion properties. Pull-out adhesion force increased with ZDA phr % in the blend; maximum force and full rubber coverage was achieved at approximately 40% ZDA. The second example demonstrates again how coagent blending of liquid and metallic (meth)acrylates can be used to optimize adhesion or tear properties while minimizing negative effects on permanent set.

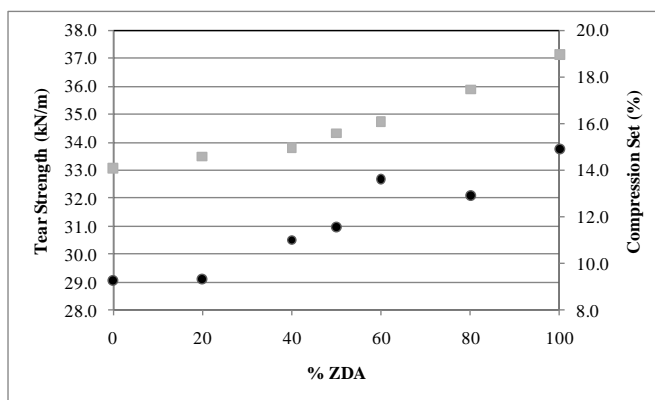


Figure 5. Tear strength (●) and compression set (■) as a function of phr % ZDA in a TA/ZDA blend; 10 phr total coagent in the EPDM model formulation.

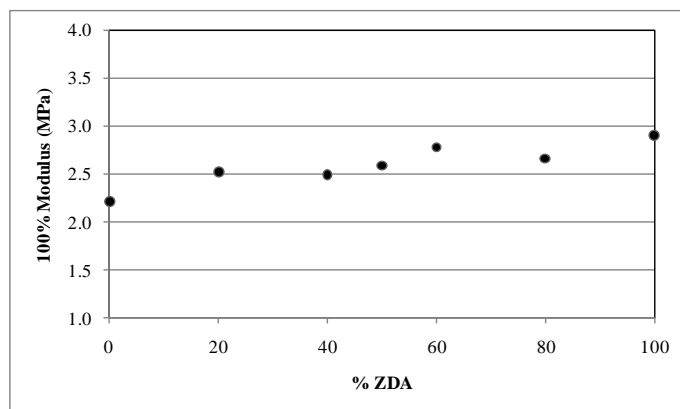


Figure 6. Modulus at 100% strain as a function of phr % ZDA in a TA/ZDA blend; 10 phr total coagent in the EPDM model formulation.

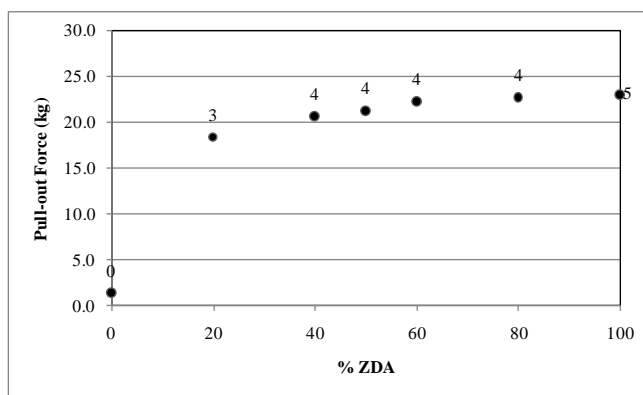


Figure 7. Pull-out adhesive force as a function of phr % ZDA in a TA/ZDA blend; 10 phr total coagent in the EPDM model formulation; brass-coated steel cord substrate. Rubber coverage scale: 0 = no rubber coverage, 5 = total rubber coverage.

Liquid-liquid blends. In many commercial applications the liquid (meth)acrylate coagents are used as reactive processing aids, often at elevated loadings to achieve the rheological targets of the process. The coagents then participate in cure, becoming fully bound to the network and non-extractable. However, these Type I coagents are highly reactive and increase crosslink density with resulting increases in hardness and modulus. In many applications high hardness is required; in others the ability to independently control hardness and other cured properties at the same coagent loadings that provide processing ease would be desired. By blending monofunctional liquid (meth)acrylates with trifunctional (meth)acrylates, it will be shown that control can be achieved.

The addition of liquid monomethacrylate (MMA) monomer decreases the efficiency of crosslinking. The monofunctional monomer is not able to effectively participate in radical addition reactions that produce elastically effective crosslinks. Instead, the likely product of MMA cure is predominantly coagent grafted to polymer. The proposed mechanism is consistent with extraction data confirming that the cured product of EPDM, MMA, and peroxide results in no extractable methacrylate monomer.

As an example, MMA was blended into TMA up to 60 phr % in the chlorinated polyethylene (CM) model formulation at a constant 10 phr total coagent loading. Lab processing indicators were measured and provided in Figure 8. Both minimum torque during the cure cycle (M_L) and uncured dynamic storage modulus (G') indicate a constant compound viscosity was maintained across the blend spectrum. In contrast, Figure 9 demonstrates that hardness was reduced to levels below that for a compound with no coagent (peroxide control) by increasing the amount of MMA in the blend. Figures 10 and 11 provide cured modulus and elongation data as a function of blend ratio. Both properties showed inversely proportional linear relationships with % MMA in the blend, effectively decreasing apparent crosslink density to levels below that of the peroxide control at the highest MMA % loading.

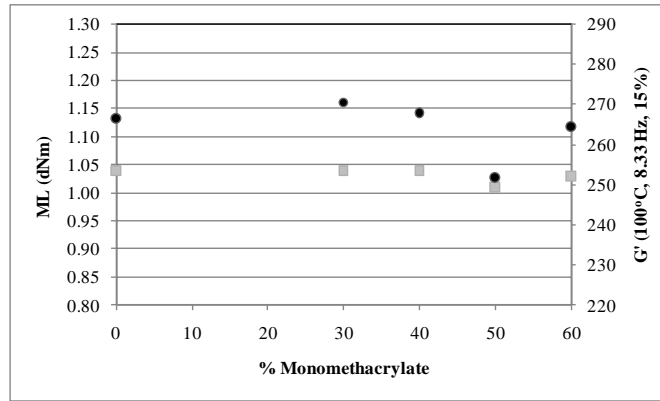


Figure 8. Processing characteristics M_L (■) and uncured G' (●) as a function of phr % MMA in a TMA/MMA blend; 10 phr total coagent in the CM model formulation.

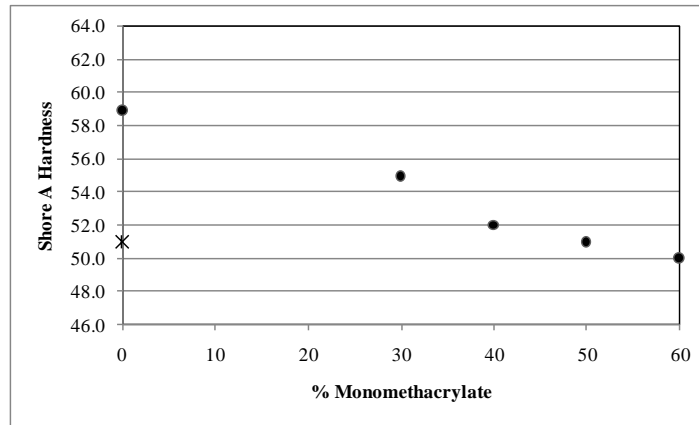


Figure 9. Shore A hardness as a function of phr % MMA in a TMA/MMA blend; 10 phr total coagent in the CM model formulation. Peroxide control (no coagent) provided for reference (x).

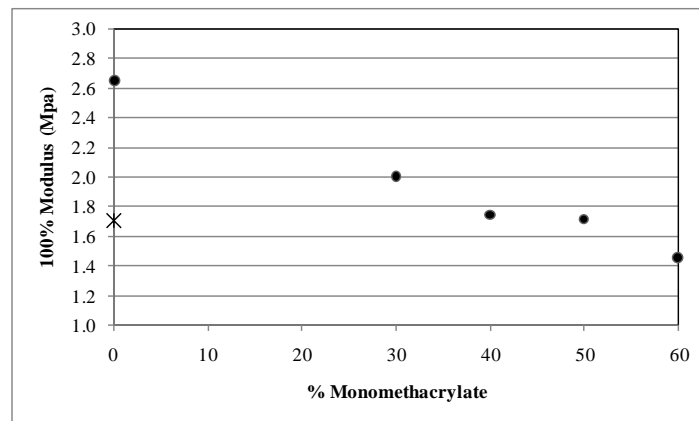


Figure 10. Modulus at 100% strain as a function of phr % MMA in a TMA/MMA blend; 10 phr total coagent in the CM model formulation. Peroxide control (no coagent) provided for reference (x).

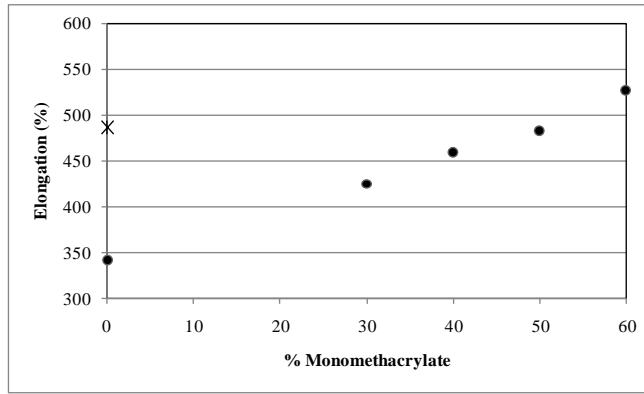


Figure 11. Elongation as a function of phr % MMA in a TMA/MMA blend; 10 phr total coagent in the CM model formulation. Peroxide control (no coagent) provided for reference (×).

Blending Acrylates with Methacrylates. It has been found that mixing acrylate-based coagents with methacrylate-based coagents does not produce desirable results. Unlike blending within a grade of coagents as in the above examples, mixing grades of (meth)acrylates generally results in negligible improvements. When mixing species, it is postulated that the kinetically more active acrylate species dominates the cure mechanism.

To illustrate the limited utility of mixed species blending, liquid acrylate (TA) and methacrylate (TMA) monomers were blended at a constant 10 phr total coagent loading in the EPDM model formulation. Figure 12 presents rheometer delta torque values as a function of phr % methacrylate in the blend. The change in value was not significant across the blend spectrum. Figure 13 compares modulus and compression set data for the same series.

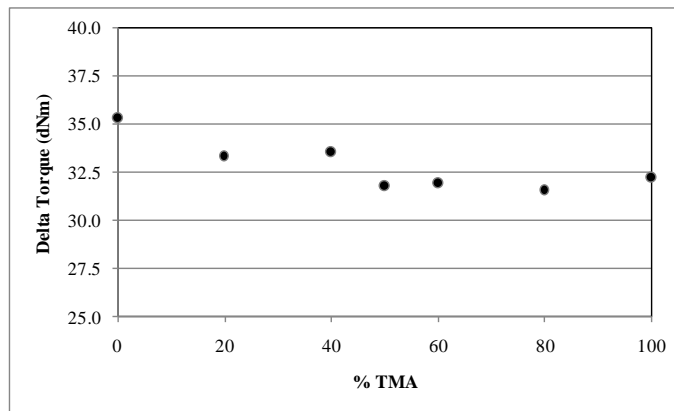


Figure 12. MDR delta torque as a function of phr % TMA in a TA/TMA blend; 10 phr total coagent in the EPDM model formulation.

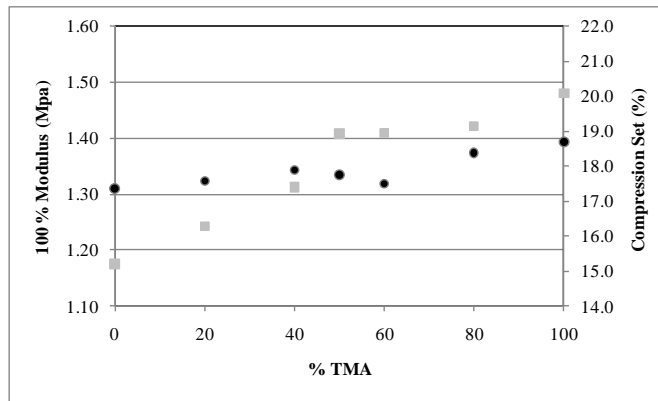


Figure 13. Modulus at 100% strain (●) and compression set (■) as a function of phr % TMA in a TA/TMA blend; 10 phr total coagent in the EPDM model formulation.

Blending Type I and Type II Coagents

Type I metallic monomers blended with Type II coagents. There are many more options for blending Type I and Type II coagents, due to the variety of Type II coagent structures available. It should be noted that many of the Type II coagents are specifically tailored for efficient peroxide cure of specialty elastomers, such as FKM, CM, and nitriles.

Presented as an example are blends of ZDA and triallyl isocyanurate (TAIC) coagents for the peroxide cure of a fluorinated elastomer (FKM) model formulation. The total coagent loading was held constant at 5 phr. TAIC is the most effective coagent for the peroxide cure of fluoroelastomer compounds, but imparts no adhesion properties. Alone, (meth)acrylates are not effective coagents for FKM. Figure 14 demonstrates that crosslink density, as measured by MDR delta torque, dropped considerably when ZDA is used as the exclusive coagent. However, delta torque is maintained with the addition of ZDA in the blend up to approximately 50 phr %. Figure 15 demonstrates the benefit of ZDA on adhesion at even low blend ratios, as 25 phr % provided the highest pull-out force and complete rubber coverage for a brass-coated steel cord substrate. The loss of adhesive force at 100% ZDA was related to the loss of cured rubber properties when ZDA is used as the exclusive coagent. The failure mode is still cohesive; pull-out force is dependent on the bulk rubber properties, not the adhesion at the rubber/cord interface. Tensile strength and compression set as a function of ZDA phr % is provided in Figure 16 for reference. Tensile strength decreases significantly at the highest ZDA loadings. Compression set was minimized at full TAIC loading, and was maintained at 25 phr % ZDA loading in the blend. As the ZDA is increased in the blend, compression set correspondingly increased. The data demonstrates that by using TAIC/ZDA blends, cured-in-place adhesion can be maximized at relatively low metallic monomer loadings that maintain tensile and compression properties associated with TAIC.

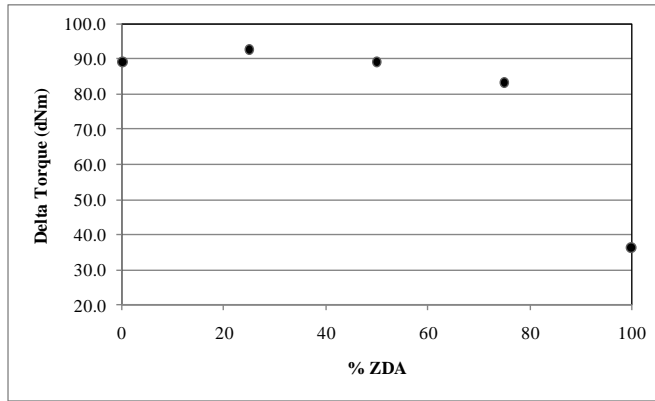


Figure 14. MDR delta torque as a function of phr % ZDA in a TAIC/ZDA blend; 5 phr total coagent in the FKM model formulation.

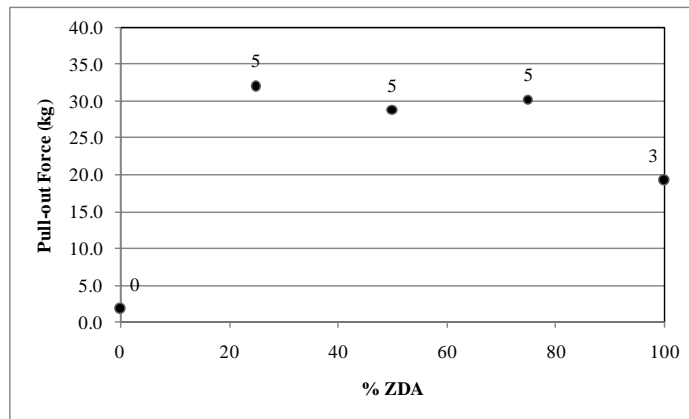


Figure 15. Pull-out adhesive force as a function of phr % ZDA in a TAIC/ZDA blend; 5 phr total coagent in the FKM model formulation; brass-coated steel cord substrate. Rubber coverage scale: 0 = no rubber coverage, 5 = total rubber coverage.

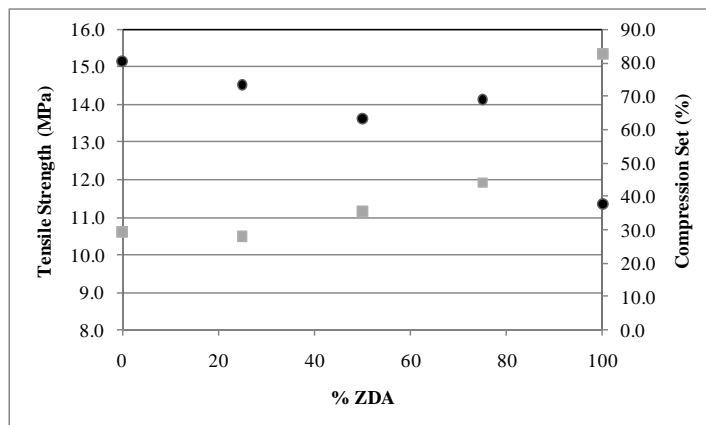


Figure 16. Tensile strength (●) and compression set (■) as a function of phr % ZDA in a TAIC/ZDA blend; 5 phr total coagent in the FKM model formulation.

Type I liquid monomers blended with Type II coagents. Scorch retarding additives are commonly used in Type I coagents to increase the scorch safety of these highly reactive monomers. However, even

when applying retarder technology the scorch times are considerably lower than Type II coagents, which are classified by their negligible impact on cure kinetics. The following examples demonstrate that the practice of blending Type I and Type II coagents can increase scorch safety to a greater extent than scorch retarding technology alone. Depending on the elastomer being cured, physical properties are affected to varying degrees.

The primary example focused on a blend of liquid methacrylate monomer and a high vinyl poly(butadiene) resin (HVPBD) in nitrile rubber (NBR), EPDM, and CM model formulations at a constant loading of 10 phr total coagent. These base elastomers are quite different in structure, and the relative contribution of each to the crosslinking mechanism will decrease as unsaturation decreases. In addition, hydrogen abstraction from the polymers also becomes more difficult. Figure 17 compares the three model formulations, looking at scorch safety (ts_2) as a function of increasing HVPBD phr % in a TMA/HVPBD blend. Note that the TMA coagent contains scorch-retarding additives. Scorch time increased with an increase in HVPBD blend concentration for the EPDM and CM formulations. However, little change was noted across the blend ratio spectrum in the NBR formulation. The results are consistent with previous studies,³ where the high reactivity of the NBR polymer itself to radical reactions dominated the cure mechanism, effectively minimizing the relative impact of different coagents. Tensile and compression measurements are provided in Figures 18 and 19, respectively. For the NBR formulation, modulus decreases as HVPBD % phr is coagent is increased, while little change in modulus is noted for the EPDM and CM compounds as a function of HVPBD concentration. Compression set is relatively constant as a function of loading for all model formulations. Note that the relatively inert quality of the CM elastomer to cure reactions is manifested in much higher permanent set values, suggesting that crosslinking reactions are almost completely limited to the coagents. These examples demonstrate that scorch safety can be increased while maintaining tensile and compression properties through a blending strategy.

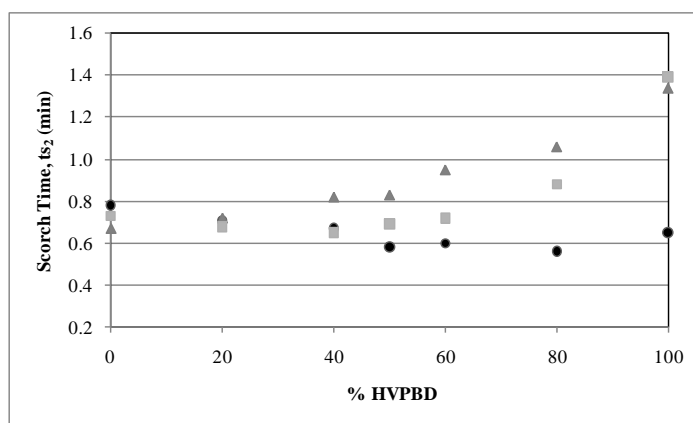


Figure 17. Scorch safety (ts_2) as a function of phr % HVPBD in a TMA/HVPBD blend; 10 phr total coagent in NBR (●), EPDM (□), and CM (■) model formulations.

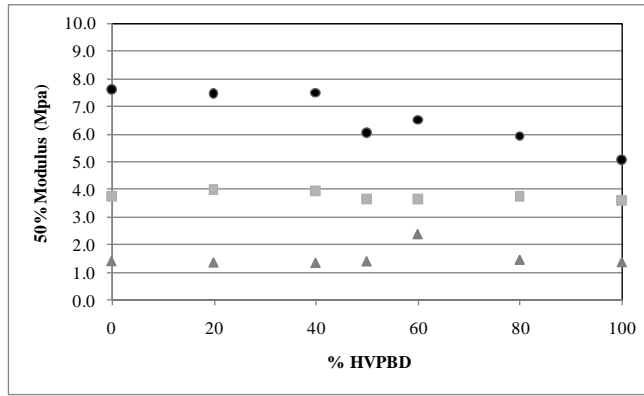


Figure 18. Modulus at 50% strain as a function of phr % HVPBD in a TMA/HVPBD blend; 10 phr total coagent in NBR (●), EPDM (□), and CM (■) model formulations.

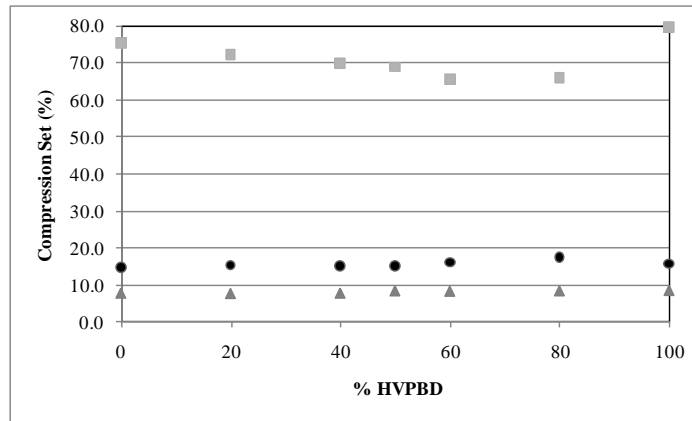


Figure 19. Compression set as a function of phr % HVPBD in a TMA/HVPBD blend; 10 phr total coagent in NBR (●), EPDM (□), and CM (■) model formulations.

A second example studies blends of triallyl cyanurate (TAC) with TMA at a constant 10 phr total coagent loading in the EPDM model formulation. Figure 20 quantifies the impact on scorch safety with increasing TAC concentration in the blend. Scorch times increased as the percentage of TAC increased. At the extremes in blend ratio, the effect was a two-fold increase in scorch time. Figure 21 demonstrates that modulus was not significantly affected by blend ratio. Figure 22 presents tear strength and compression set values as a function of TAC phr % in the blends. Despite near constant modulus across the blend spectrum, the compression set was decreased and tear strength reduced as TAC concentration was increased. The example demonstrates that scorch time and compression set may be improved at intermediate TAC blend ratios while balancing tear strength.

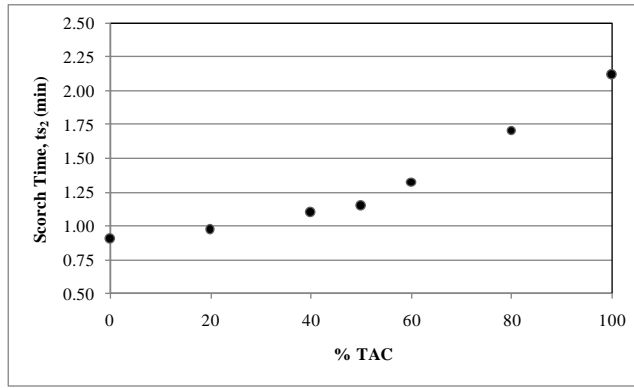


Figure 20. Scorch safety (ts_2) as a function of phr % TAC in TMA/TAC blends; 10 phr total coagent in the EPDM model formulation.

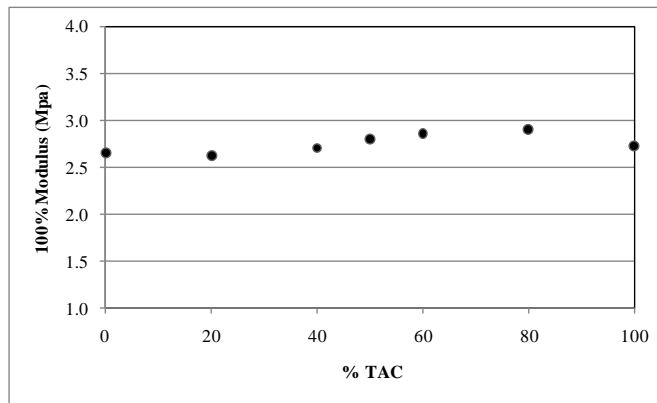


Figure 21. Modulus at 100% strain as a function of phr % TAC in TMA/TAC blends; 10 phr total coagent in the EPDM model formulation.

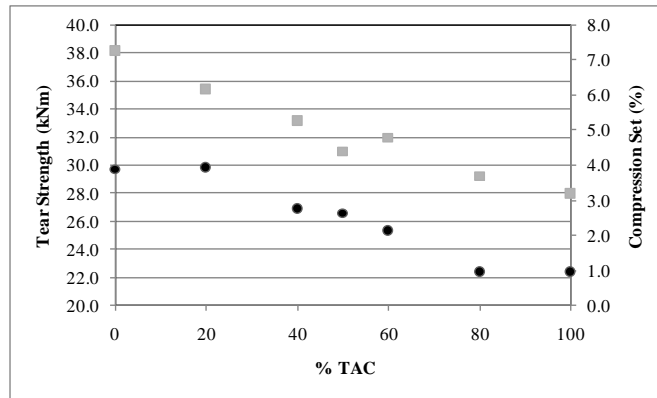


Figure 22. Tear strength (●) and compression set (■) as a function of phr % TAC in TMA/TAC blends; 10 phr total coagent in the EPDM model formulation.

An additional example highlights blends using phenylene dimaleimide (PDM) as the Type I coagent. The PDM monomer is unique in its activity. Empirical evidence suggests that addition reactions between PDM monomers are not favored, limiting the monomers ability to homopolymerize. It is thought that direct reaction with polymer radicals and crosslinking through grafting reactions comprise

the primary cure mechanism. Alternatively, the PDM coagent can also react with in-chain unsaturation through ionic mechanisms in the absence of radicals.⁸ If true, any benefits from a blending strategy may be diminished.

PDM blends are studied in the HNBR model formulation at constant 10 phr total coagent loading. PDM/HVPBD blends are examined, and PDM/TMA blends (a Type I monomer blend) is included for comparative purposes. Figure 23 shows the trend in scorch safety as a function of blend ratio for each system. Increased scorch safety was seen with increasing blended monomer, but the magnitude of change for the PDM blends was not as large compared with the previous examples. Figures 24 and 25 provide modulus and compression set data, respectively. Both properties are degraded significantly with increasing blended coagent phr %. The data from the present example supports the independent cure mechanism hypothesized for the PDM Type I monomer. Blending does not provide significant changes in scorch safety, and cured physical properties are not balanced as seen in previous examples.

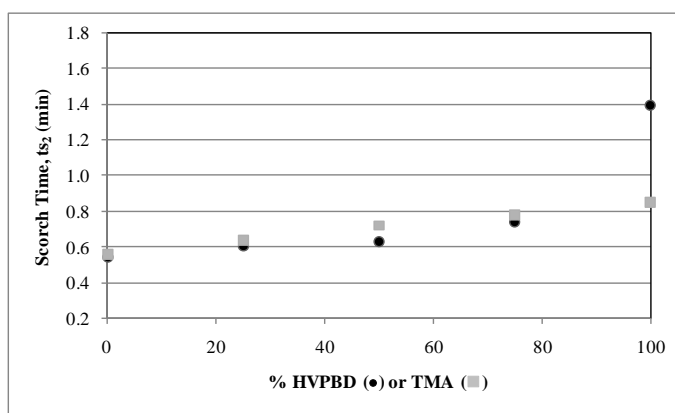


Figure 23. Scorch safety (ts₂) as a function of second coagent in both PDM/HVPBD (●) and PDM/TMA (■) blends; 10 phr total coagent in the HNBR model formulation.

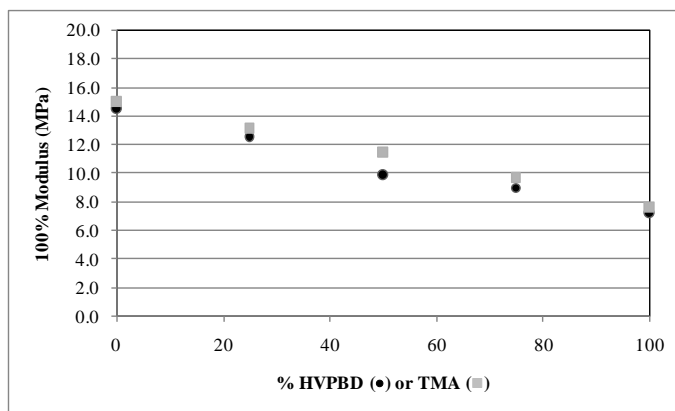


Figure 24. Modulus at 100% strain as a function of second coagent in both PDM/HVPBD (●) and PDM/TMA (■) blends; 10 phr total coagent in the HNBR model formulation.

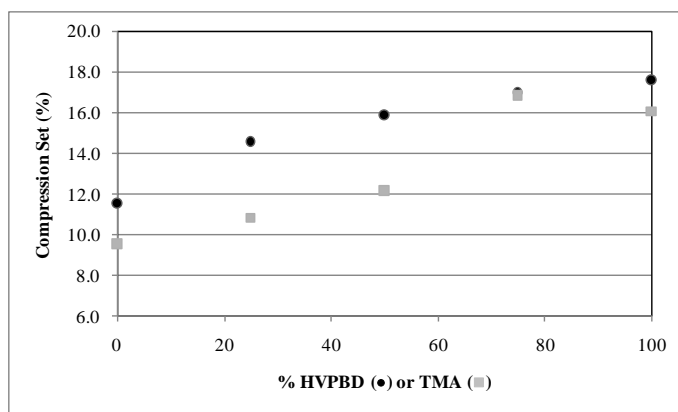


Figure 25. Compression set as a function of second coagent in both PDM/HVPBD (●) and PDM/TMA (■) blends; 10 phr total coagent in the HNBR model formulation.

SUMMARY AND CONCLUSIONS

Binary blends of coagents can be applied to peroxide cured elastomer compounds to balance cure kinetics, processing, and cured physical properties. In many cases, physical properties that would be mutually exclusive can be optimized through blend strategies. By blending liquid (meth)acrylate monomers with metallic (meth)acrylate monomer grades, cured-in-place adhesion can be achieved at relatively low concentrations of metallic monomer in the blend, greatly reducing the negative impact on permanent set. Monofunctional liquid (meth)acrylates can be blended with multifunctional grades to independently control cured physical properties while maintaining high overall coagent loading and desired processing characteristics. In many cases, Type II coagents can be blended with Type I grades to provide greater improvements in scorch safety for a variety of specialty elastomers, while balancing cured tensile and compression properties. Specifically, metallic monomer/Type II coagent blends can be applied to achieve adhesion properties while maintaining physical properties in specialty elastomer grades. In most cases the compound properties are linearly correlated with blend ratio, providing a predictive tool based on additive coagent contribution to the cured network.

Several blending rules were established. When blending Type I monomers, beneficial results were obtained with (meth)acrylate monomers having the same reactive functionality, ie. acrylates with acrylates or methacrylates with methacrylates. In general, Type I and Type II monomers can be blended to balance specific properties, with the notable exception of blends with PDM.

Appendix.
Model formulations.

EPDM Masterbatch	
Ingredient	phr
EPDM	100
N660 Carbon Black	100
Sunpar® 2280	50
Stearic Acid	1
total	251

FKM Masterbatch	
Ingredient	phr
FKM	100
MT990 Carbon Black	30
ZnO	5
VPA #2	1
total	136

CM Masterbatch	
Ingredient	phr
CM	100
N550 Carbon Black	60
CaCO ₃	40
DIDP	30
Maglite® D	5
Agerite® Resin D	1
total	236

NBR Masterbatch	
Ingredient	phr
NBR	100
N550 Carbon Black	50
PlastHall® 7050	5
Stearic Acid	1
Agerite® Resin D	1
total	157

HNBR Masterbatch	
Ingredient	phr
HNBR	100
N550 Carbon Black	50
TOTM	5
total	155

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- ⁶ S. X. Guo and W. von Hellens, *Rubber World* **225** (5), 51 (2002).
- ⁷ L. H. Palys and P. A. Callais, *Rubber World* **229**(3), 35 (2003).
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